Development of an orthodontic elastic material using EMA-based resin combined with 1-butanol

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For the development of new orthodontic elastic material, 1-butanol was added to PEMA-TA/HX resin. In the present study, basic experiments to reveal the mechanical properties of the materials were conducted. FT-IR spectroscopy showed that addition of 1-butanol did not cause any chemical changes to the PEMA-TA/HX resin. After addition of 1-butanol to PEMA-TA/HX resin, the modulus of elasticity, instantaneous modulus elasticity, retarded elasticity and viscosity were lowered in a concentration-dependent manner, whereas the elastic strain was increased in a concentration-dependent manner. Moreover, on the application of heat a shape-memory effect was observed. These results suggest that the modulus of elasticity of this material can be adjusted. Additionally, this material has the ability to restore force as a function of its shape-memory effect in cases of plastic deformation at the insertion of appliances. This new orthodontic elastic material has the potential to be clinically effective in orthodontic treatment.

Keywords: Resin, Shape-memory, 1-butanol

INTRODUCTION

Orthodontic elastic materials are superior to multibracket appliances from an esthetic standpoint because of their translucency, drawing the attention of clinicians and researchers to these materials for use in removable appliances used for adults with high esthetic demands1,2). Some studies have reported that, since these materials do not require bracket application on the tooth surface, brushing of teeth is easier than with conventional appliances, reducing the prevalence of dental caries and periodontal diseases3-6). Nevertheless, the physical properties of current orthodontic elastic materials include intermittent force application and no shape-memory effect, unlike the Ni-Ti wires used in multibracket appliances, indicating that these materials are not yet suitable for use in orthodontic appliances.

First of all we searched for additives that would allow for adjustment of the modulus of elasticity. There is concern over plasticizers such as phthalates, which are known to be endocrine-disrupting7), indicating their inadequacy for use in the oral environment. Of these softeners, addition of alcohol to acrylic resin adjusts the modulus of elasticity; some studies have reported that when ethyl alcohol is added in the resin, distortion is removed by application of heat, even after permanent strain8). Based on these reports, we selected 1-butanol as a softener, which is added to alcoholic beverages and food as a fragrance. As a base resin, polyethyl methacrylate-methacryloyloxyethyl methyl succinate/1,6-hexanediol dimethacrylate resin (PEMA-TA/HX resin) was selected, which is currently under development for use in transplants8,10). In this study, using these materials, we conducted basic experiments to reveal the mechanical properties of the materials and develop safe orthodontic elastic materials with the changeable modulus of elasticity.

MATERIALS AND METHODS

Composition of PEMA-TA/HX resin
Polyethyl methacrylate (PEMA; Syofu, Kyoto, Japan) was used as the powder component with addition of 1.2 wt% benzoyl peroxide (Syofu, Kyoto Japan). In the liquid component, 0.75 wt% N,N-dimethyl-p-toluidine (Syofu, Kyoto, Japan) was added to a mixture of 40 wt% methacryloyloxyethyl methyl succinate (TA; Syofu, Kyoto, Japan) and 59.25 wt% 1,6-hexanediol dimethacrylate (HX; Syofu, Kyoto, Japan) to fabricate the PEMA-TA/HX monomer. PEMA-TA/HX resin was fabricated by polymerizing this powder and liquid for 1 hour at 27°C (Table 1).

Adjustment of the polymerized sample material
The standard powder and liquid ratio of PEMA-TA/HX polymer and monomer was set at 3 g/1.89 g. Since incomplete polymerization occurs if the monomer is 1.89 g or less, 1-butanol (Kanto Chemical, Tokyo, Japan) was added to adjust the concentration of 1-butanol to 10, 20, 30, and 40%, as well as a 0% sample (samples B-0, B-10, B-20, B-30, and B-40) (Table 2). The temperature during all testing was set at 27°C.

Measurement by Fourier-transform infrared spectroscopy
After polymerization of B-0 and B-40 samples, they were ground and mixed with the KBr tablet. Then, the Infrared spectra on day 0 and after 28 days were measured to examine the chemical reaction between 1-butanol and PEMA-TA/HX resin. For this measurement, FT-IR spectroscopy (Diamond-20, JEOL,
Tokyo, Japan) was used with 32 accumulation times.

Measurement of weight changes over time
Samples of B-0, B-10, B-20, B-30, and B-40 were poured in a mold (height, 12 mm; diameter, 6 mm). After polymerization, each sample was placed in an uncovered small bottle and stored in an incubator at 37°C. The weight of samples was measured using an electric weighing machine (Sartorius AG, Goettingen, Germany) every 24 hours for 28 days to observe the changes. The room temperature during measurement was set at 27°C.

Measurement of the modulus of compressive elasticity
Samples of B-0, B-10, B-20, B-30, and B-40 were poured into a mold of 12 mm height and 6 mm diameter and then after polymerization they were stored in water in an incubator at 37°C. Compression testing was conducted using a universal testing machine (Instron 4481, Instron Japan, Kawasaki, Japan) at a crosshead speed of 1 mm/min. After obtaining stress/strain curves, the modulus of compressive elasticity (measured in MPa) was calculated. In addition, the same testing was performed after soaking the samples in water for 28 days to compare the results. The room temperature during measurement was set at 27°C. The sample size was n=5 in each group. Comparison among each group was conducted by multiple-comparison tests using the Bonferroni procedure.

Measurement of elastic strain and permanent strain
Samples of B-0, B-10, B-20, B-30, and B-40 were poured into a mold of 20 mm height and 13.0 mm diameter and then after polymerization they were stored in water in an incubator at 37°C. An apparatus for constant-strain testing (A-002, Toyama, Japan) was used to measure the elastic strain and permanent strain of the samples. Placing the sample on a plunger (9,806.7 Pa), the number presented on a dial gauge after 30 seconds was defined as A (mm). After another 30 seconds, 88,260.3 Pa of stress was applied to the sample over the course of 10 seconds (total 98,067 Pa of stress). Then, after 20 seconds the number on the gauge was read and defined as B (mm). Simultaneously, 88,260.3 Pa of the load was removed and, after 60 seconds, C (mm) was obtained (see Fig. 1). After obtaining the aforementioned values the elastic strain and permanent strain were calculated using equations 1 and 2.

![Fig. 1 Scheme showing steps in the measurement of elastic strain and permanent strain.](image)

<table>
<thead>
<tr>
<th>Elastice strain (%)</th>
<th>Permanent strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{B-(mm)-A-(mm)}{\text{sample height (mm)}} \times 100 )</td>
<td>( \frac{C-(mm)-A-(mm)}{\text{sample height (mm)}} \times 100 )</td>
</tr>
</tbody>
</table>

Table 1 Compositions of PEMA-TA/HX resin

<table>
<thead>
<tr>
<th>Component</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid</td>
<td>40 wt% methacryloxyethyl methyl succinate(TA)</td>
</tr>
<tr>
<td></td>
<td>59.25 wt% 1,6-hexanediol dimethacrylate(HX)</td>
</tr>
<tr>
<td></td>
<td>0.75 wt% N,N-dimethyl-p-toluidine</td>
</tr>
<tr>
<td>Powder</td>
<td>98.8 wt% polyethyl methacrylate(PEMA)</td>
</tr>
<tr>
<td></td>
<td>1.2 wt% benzoyl peroxide</td>
</tr>
</tbody>
</table>

Table 2 Compositions of each sample

<table>
<thead>
<tr>
<th>Code</th>
<th>Powder</th>
<th>Monomer</th>
<th>1-butanol</th>
<th>wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-0</td>
<td>3.00 g</td>
<td>1.89 g</td>
<td>0 g</td>
<td>0%</td>
</tr>
<tr>
<td>B-10</td>
<td>3.00 g</td>
<td>1.89 g</td>
<td>0.21 g</td>
<td>10%</td>
</tr>
<tr>
<td>B-20</td>
<td>3.00 g</td>
<td>1.89 g</td>
<td>0.47 g</td>
<td>20%</td>
</tr>
<tr>
<td>B-30</td>
<td>3.00 g</td>
<td>1.89 g</td>
<td>0.81 g</td>
<td>30%</td>
</tr>
<tr>
<td>B-40</td>
<td>3.00 g</td>
<td>1.89 g</td>
<td>1.26 g</td>
<td>40%</td>
</tr>
</tbody>
</table>

“wt%” indicates the proportion of 1-butanol in the total liquid weight (monomer and 1-butanol).
**Measurement of shape-recovery ratio**

Samples were fabricated by pouring B-40 into a mold of 12 mm height (H0) and 6 mm diameter. After polymerization they had been stored in water in an incubator at 37°C for 28 days. After compressing the samples to half of their height (H1) in a universal testing machine (Instron 4481, Instron Japan, Kawasaki, Japan), they were soaked in a constant-temperature bath at 37, 50, or 60°C for 1, 3, 5, 7, or 9 minutes, after which their new height, H2, was measured. Thereafter, the shape-recovery ratios were calculated using equation 3.

\[
\text{Shape-recovery ratio} = \frac{(H_2 - H_1)}{(H_0 - H_1)} \times 100 \quad \text{(eqn 3)}
\]

The room temperature during measurement was set at 27°C. Considering the cases of drinking hot water, the highest temperature was set at 60°C. Comparison among each group was conducted by multiple-comparison tests using the Bonferroni procedure.

**Viscoelasticity**

Samples of B-0, B-10, B-20, B-30, and B-40 were poured into a mold of 20 mm height and 13 mm diameter and polymerized, and then stored in water in an incubator at 37°C for 24 hours. Using a universal testing machine (Instron 4481, Instron Japan, Kawasaki, Japan), 2.0 mm of initial displacement was instantly rendered and changes in stress were recorded for 15 minutes. The room temperature during measurement was set at 27°C. For the analysis, a viscoelastic three-element-solid model11) was used because there was no significant difference between the models with more than four elements and the former in a previous study (Fig. 2).

The following three analysis parameters were used for viscoelastic testing (where E1 and E2 indicate the modulus of elasticity of A1 and A2, respectively, and \(\eta\) indicates the viscosity of B):

- **Instantaneous modulus elasticity:** \(E_1 + E_2\)
- **Retarded elasticity:** \(E_2\)
- **Viscosity:** \(\eta\)

In the testing of viscoelasticity presented in Fig. 3, the time immediately after 2.0 mm displacement by loading was defined as \(\tau=0\), the initial stress at that time as \(\sigma_0\), the stress 900 seconds after loading as \(\sigma_{900}\), and initial strain as \(\varepsilon_0\). The dashpot B (see Fig. 2), representing viscoelastic parts, does not function immediately after strain application. In this situation, the initial stress can be expressed in equation 4.

\[
\sigma_0 = (E_1 + E_2)\varepsilon_0 \quad \text{(eqn 4)}
\]

The stress after 900 seconds can be expressed shown in equation 5.

\[
\sigma_{900} = E_2 \cdot \varepsilon_0 \quad \text{(eqn 5)}
\]

\(\sigma_0\) and \(\sigma_{900}\) were obtained by measurement, whereas \(\varepsilon_0\) was calculated by subtracting the amount of displacement from the height of the samples. \(E_1\) and \(E_2\) were calculated by substituting the values above into the equation. \(\eta\) was obtained from the equation below.

\[
\sigma = E_2 \cdot \varepsilon_0 + E_1 \cdot \varepsilon_0 \exp\left[-\left(\frac{E_1}{\eta}\right)t\right] \quad \text{(eqn 6)}
\]

In all testing, the sample size was \(n=5\) in each group. Comparison between the control and experimental groups was performed using Student’s t-test. Comparison among each group was conducted by multiple-comparison tests using the Bonferroni procedure.
RESULTS

**Measurement by Fourier-transform infrared spectroscopy**
The C=C, C–C, and C=O absorption bands appeared at 1,600–1,800, 800–1,300, and 1,650–1,800 cm\(^{-1}\), respectively. However, differences in the infrared spectra between samples of B-0 and B-40 were not observed. In addition, no changes were found in the infrared spectra between days 0 and 28 of the experiment (Fig. 4).

**Measurement of weight changes over time**
The control group (B-0) showed a constant value regardless of the time; in contrast, the experimental groups with 1-butanol (B-10, B-20, B-30, and B-40) showed a decrease in weight over time. The extent of the decrease in weight was proportional to the amount of 1-butanol in the resin. In all of the samples the rate of decrease started to decline after around 5 days; however, even after 28 days the decline in weight had not stopped, with constant values not being exhibited by this time point (Fig. 5).

**Measurement of the modulus of compressive elasticity**
By adding 1-butanol, significant differences were found in samples of each group after 1 day and 28 days, showing decrease of compressive elasticity in a concentration-dependent manner. In samples of B-0 there was almost no difference between 1-day and 28 days time points, but the other groups showed significantly higher values after 28 days (Fig. 6).

**Measurement of elastic strain and permanent strain**
Elastic strain was observed to increase in a concentration-dependent manner in relation to 1-butanol concentration of the sample (Fig. 7). As with elastic strain, the more 1-butanol present in a sample, the higher the value of permanent strain presented (Fig. 8).

**Measurement of shape-recovery ratio**
The distortion generated by compression of samples was examined after they had been stored in water at 37°C for 28 days. An increase in the shape-recovery ratio — meaning recovery of samples to a shape approximating their initial form — was observed when the temperature of the soaking solution increased. Specifically, for a 1-minute soaking time, a shape-recovery ratio of only 13.4% was obtained at 37°C, whereas ratios of 75.7 and 91.3% were observed at 50 and 60°C, respectively. After 3, 5 and 7 minutes, shape-recovery ratios showed an increasing tendency at all tested temperatures. On soaking for 9 minutes, shape-recovery ratios of nearly 100% were achieved at 50 and 60°C, whereas only 50.2% shape recovery was observed at 37°C for the same time (Fig. 9). These results suggest that the shape-memory effect of this material is achieved by application of heat.

**Viscoelasticity**
According to the stress-time curves, in all samples most of stress that had been applied disappeared by 60 seconds. By 15 minutes (900 seconds) after loading the
values were leveling-off to constant values, although still with a tendency to decrease gradually, thus illustrating asymptotic elastic behavior (Fig. 10).

$E_1 + E_2$ (instantaneous modulus elasticity) decreased in a concentration-dependent manner as the amount of 1-butanol (Fig. 11). Similarly, $E_2$ (retarded elasticity) decreased in accordance with an increased concentration of 1-butanol; however, no significant difference between B-30 and B-40 was observed (Fig. 12). Viscosity ($\eta$) also decreased as the amount of 1-butanol increased (Fig. 13). No significant difference was found between samples B-30 and B-40.
DISCUSSION

There was a concern about the possibility of chemical reaction with the addition of 1-butanol to PEMA-TA/HX resin, but there was no such reaction, indicating the existence of 1-butanol among molecules of resin. Therefore, addition of 1-butanol that can be broken down in vivo with PEMA-TA/HX resin seems to be unproblematic compared with other resins. Plasticizers were known to enlarge the distance between chains of the polymer and weaken intermolecular force to soften the polymer. It is suggested that 1-butanol has the same effects with that. Although it is impossible to adjust the uniform modulus of elasticity in conventional orthodontic elastic materials, by addition of 1-butanol to PEMA-TA/HX resin it would be possible to control the modulus of compressive elasticity, elastic strain, retarded elasticity considering time factors, and viscoelasticity.

One study has reported that the moduli of elongation of various current orthodontic elastic materials ranged between about 150 and 650 MPa, whereas that of a tooth positioner made of silicon rubber-type material was about 4.5 MPa. In the present study, samples B-0 and B-40 showed moduli of compressive elasticity of about 740.7 and 7.1 MPa, respectively. Since the moduli of elongation and compressive elasticity are suggested to approximate each other in viscoelastic bodies such as the samples in the present study, our values are in the range of the previous study. Another study reported that the instantaneous modulus elasticity, retarded

Fig. 10 Stress-time curve in relation to 1-butanol concentration after 1 day. X-axis: Time Y-axis: Stress

Fig. 11 Instantaneous modulus elasticity obtained after viscoelastic testing of B-0, B-10, B-20, B-30 and B-40 samples after 1 day. **p<0.01; *p<0.05

Fig. 12 Retarded elasticity. **p<0.01

Fig. 13 Viscosity. **p<0.01; *p<0.05
elastomer and viscosity of silicone rubber materials were approximately 15.0 MPa, 1.5 MPa and 3.2 MPa/sec, respectively\(^{10}\). They showed values close to our value for the B-40 sample, although their values were slightly lower than ours. Since the retarded elasticity and viscosity showed elastic deformation and flowability over time, respectively, the B-40 sample was considered to have the almost same level of the elastic deformation and flowability over time with silicon-rubber type material. In addition, since the instantaneous modulus of elasticity was higher than that of silicon-rubber type material, almost none of elastic deformation immediately after loading may occur.

Based on these data, it is suggested that, in terms of intermittent and continuous forces, the physical properties of our proposed material can be adjusted to match those of clinically used orthodontic elastic materials and tooth positioners, as appropriate. Moreover, the movement distance of teeth can be increased by reduction of the modulus of elasticity when appliances are fabricated from this new material. Retention of appliances using undercuts of teeth may provide an improvement in rotated teeth and bodily movement relative to conventional orthodontic elastic materials. Another advantage of this material is that by addition of 1-butanol the modulus of compressive elasticity and the instantaneous modulus elasticity are decreased, thus alleviating the pain associated with insertion of conventional orthodontic elastic materials due to strong orthodontic forces being applied. Since measurement of time-dependent weight changes becomes difficult when samples absorb water, measurement was conducted without water immersion unlike the condition of testing of compressive elasticity and others. However, gradual evaporation of 1-butanol after polymerization was observed. Therefore, it is possible that the samples after 28 days showed evaporation of 1-butanol at measurement of compressive elasticity. This evaporation of 1-butanol may have caused gradual hardening of elastic samples. Although elastic modules show reduction of orthodontic force due to tooth movement and permanent strain, this material property may help the resin to apply continuous orthodontic force to teeth. As time advances, and the modulus of elasticity increases because of vaporization of 1-butanol, a reduction in orthodontic force will be prevented even after tooth movement.

If a viscoelastic body is compressed beyond its elastic limit, then permanent strain occurs, as shown by the results of this study (Fig. 8). However, it was revealed that by the application of heat energy this resin can almost recover its original shape, as the shape-recovery ratio was almost 100% at 50 and 60°C, representing a shape-memory effect as seen with Ni-Ti wires. This effect may be observed when drinking hot water.

The mechanism of the shape-memory effect may be explained by molecular movement tending to occur in resin samples containing 1-butanol, with easy recovery to its stable state after polymerization through heat application\(^{15}\). Additionally, the reason for the high shape-recovery rate on high-temperature soaking is considered to be more rapid activation of molecular movement as the temperature is raised. Our viscoelasticity data show that addition of 1-butanol will allow the retarded elasticity and viscosity of this resin to be altered, and thus continuous orthodontic force could be applied arbitrarily to teeth after insertion of an appliance. As the amount of 1-butanol increases, the viscosity is emphasized. As a result, irreversible plastic deformation tends to occur on general viscoelastic bodies causing difficulty in the application of orthodontic force in dental appliances. On the contrary, with our resin material even the B-40 sample, showing the highest permanent strain, recovered its original dimensions because of the shape-memory effect. This result suggests that the shape-memory effect occurs even after plastic deformation by insertion, generating effective orthodontic force. Heat energy will be applied to the appliance after insertion whenever hot drinks are ingested.

It is also possible to vary the amount of 1-butanol in resin used in the posterior and anterior regions of the mouth: in the posterior part of the appliance a high modulus of elasticity can function as an anchor, whereas in the anterior part a low modulus will provide greater tooth movement than normal with effective orthodontic force due to the shape-memory effect. Moreover, since the modulus of elasticity of this material increases over time during the tooth-moving process, a targeted amount of tooth movement will be achieved easily without reduction of orthodontic force. In addition, maladaptation of appliances on the next insertion can be minimized, suggesting new application methods that are impossible with conventional appliances.

In orthodontic treatment, appliances with a low modulus of elasticity are fabricated in cases of severe crowding requiring a large amount of tooth movement, whereas appliances with a high modulus are needed to enhance retentive effects in cases of detailing requiring a small amount of tooth movement. In this new material the amount of tooth movement can be determined arbitrarily because the modulus of elasticity is controllable; the targeted distance of tooth movement in each appliance can be controlled by a time-dependent increase in orthodontic force and shape-memory effect. These properties will reduce the frequency of appliance replacement and contribute to the achievement of a high level of treatment. However, investigations into the optimal modulus of elasticity and orthodontic force for anterior and posterior teeth, and basic research and clinical evaluation of the amount of orthodontic force during activation of shape-memory effect, are needed prior to the clinical application of this new material. Despite this requirement for further study, this material is considered to have a broad range of application for new appliances.

**CONCLUSION**

We have developed a new orthodontic elastic material with an adjustable modulus of elasticity depending on
the treatment purpose and a shape-memory effect, allowing application of appropriate orthodontic force. The following conclusions were reached.

1. Addition of 1-butanol did not cause any chemical changes in PEMA-TA/HX resin.
2. Since the modulus of elasticity is altered by changing the amount of 1-butanol, fabrication of orthodontic elastic materials with different moduli of elasticity in arbitrary areas is possible.
3. Since the modulus of elasticity of this material increases time-dependently, there is a possibility that an initially weak orthodontic force will increase over time, and that the force will not decrease even after tooth movement.
4. A shape-memory effect is expected by application of heat energy even after plastic deformation at the time of insertion, allowing the application of an effective orthodontic force to teeth.

REFERENCES